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PREPARATION OF ACTIVATED  
CARBON FILLED POLY(URIDYLIC ACID)  
MULTIFILAMENT - A SUMMARY REPORT

AMERICAN INTERNATIONAL COMPANY

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A sorbent textile yarn was developed as a potential answer to the need for comfortable and durable chemical protective clothing. The yarn was prepared with an activated carbon slurry in triethylene glycol and a blend of polypropylene and wax. These are pumped and metered in separate streams into a 12-hole hollow needle-in-orifice-type multifilament hollow fiber spinneret. The extruded hollow filament with the blend as the walls and the slurry as the core is spun down a 15-foot cooling stack and taken up conventionally with about 100:1 spin draw ratio or greater. The yarn is then drawn 5:1 at 100°C in an			

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oven at  $\sim$  350 ft/min take-up speed. Extraction of the triethylene glycol and wax was carried out successively with pentane, methanol and again pentane. The yarns produced contain 10 filaments with a total denier between 60 and 75 which corresponds to an average of 6.6 denier/filament. The diameter of the individual filaments is about 0.002 inch. The tenacity is about 2gpd and the elongation about 30%. Permeability rate through the walls of the filaments is 3000 g/m<sup>2</sup>/day for water vapor and much higher for carbon tetrachloride and methanol. Absorption capacity of the yarns for carbon tetrachloride is generally about 40%. In a dynamic flow test where the yarns were arranged on a screen and there were many open areas between yarns, the capacity for dimethoxymethyl phosphonate (DMMP) was 0.253 g/g of yarn. This represents 50% or more of the DMMP to which the yarn was exposed. Exposure time was 60 to 70 minutes. These data show the high potential of the yarn for conversion into a textile fabric for use in chemical protective clothing.

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FOREWORD

In 1970, personnel of this Command initiated the principle of filling hollow fibers with activated carbon for potential applications in chemical protective clothing and performed laboratory experiments which looked encouraging. A small services contract was then awarded to Fabric Research Laboratories (now named FRL - an Albany International Company). This effort produced samples of fiber which proved the feasibility of pumping an activated carbon slurry into a hollow fiber. However, physical properties of the filled fiber were not satisfactory. The current contract was awarded through the open bid process to extend this work, not only to improve the physical properties of the filled fiber but also to improve the preparation process. The effort was supplemented by a subcontract to MSA Research Corporation for analytical services. Dr. Richard N. Macnair was the Contracting Officer's Representative.

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PREPARATION OF ACTIVATED CARBON-FILLED MICRO-  
POROUS HOLLOW MULTIFILAMENT - SUMMARY REPORT

Myron J. Coplan and George Lopatin

INTRODUCTION

The highly absorbent multifilament textile yarns produced under this contract are a stage in the development of a durable protective uniform that will offer protection against aerosol dispersed CW agents. Military clothing must be sufficiently comfortable and robust to be practical for prolonged use in the field. Existing technology utilizes either active carbon impregnated materials, which are uncomfortable and impose too great a heat stress on the body, or active carbon fibers which are very friable with low extensibility and almost no abrasion resistance.

A yarn that could withstand the stresses of processing into fabrics, be fine, durable, and extensible enough to impart satisfactory "hand," abrasion resistance, and strength to a clothing fabric, namely, be a textile yarn and be sufficiently sorbent to offer sufficient protection against CW agents, is clearly needed. To develop and produce such a yarn was the goal of this program. The process and its development which have produced a yarn that appears to satisfy these requirements are discussed in this report.

SUMMARY OF PROCESS

Materials Preparation

A slurry is made by dispersing active carbon, Amoco PX21, pulverized to <325 mesh, in triethylene glycol (TEG) with a colloid mill. Additional carbon is added during the milling to about 25% by weight total loading. The slurry is sieved through a 200-mesh screen. Prior to extrusion, it is heated to 180°C under a nitrogen gas sweep to remove low boiling constituents.

A polymer blend is prepared by melt-blending polypropylene, Hercules 6523, and paraffin wax (MP  $\sim$  55°C) at 30% by weight of wax, extruding the blend through an 80 micron filter, and grinding it to a powder.

#### Spinning

The two materials, blend and slurry, are pumped and metered in separate streams into a 12-hole hollow needle in orifice-type multi-filament hollow fiber spinneret of FRL design and extruded at  $\sim$  170°C (orifice diameter = 0.070"). The extruded hollow filament with the blend as the wall and the slurry as the core is spun down a 15-foot cooling stack and taken up conventionally with about 100:1 spin draw or greater. The yarn is then drawn 5:1 at 100°C in an oven at  $\sim$  350 ft/min take-up speed.

#### Extraction

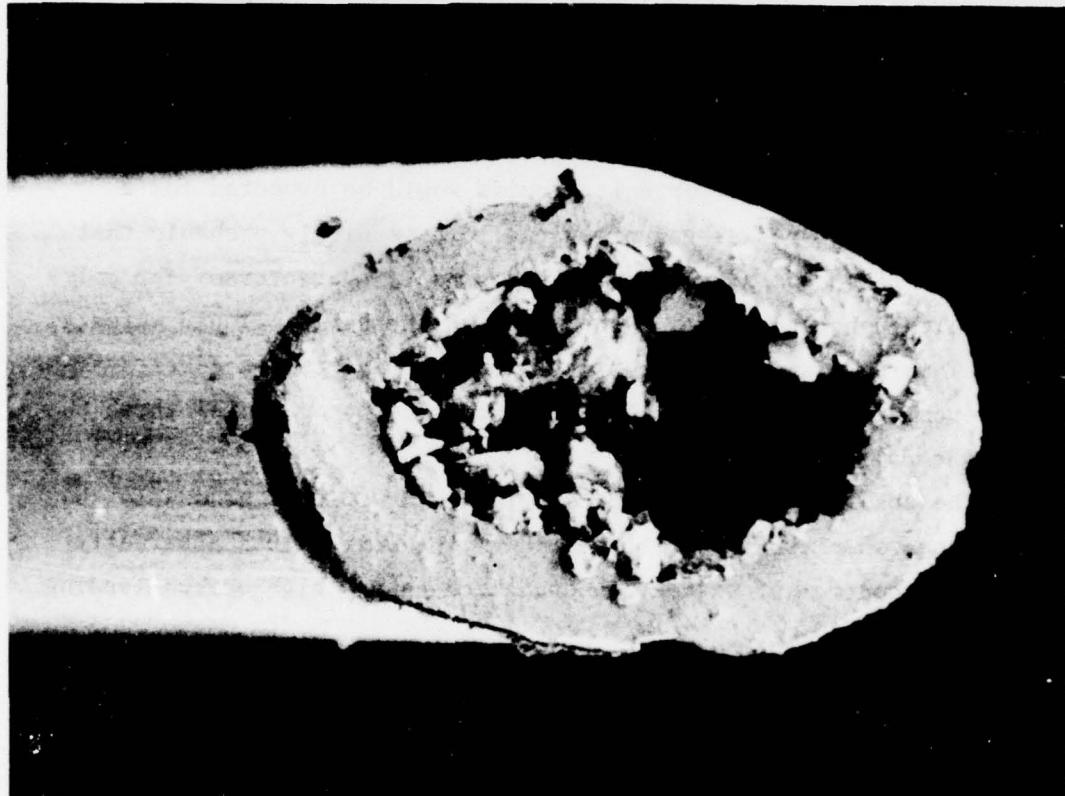
The drawn yarn can either be extracted as a yarn or processed into a fabric, in which case the fabric would be extracted. The yarns shrink considerably if not restrained during extraction, which poses problems with large samples. The extraction steps as they have been developed to date are:

1. A room temperature pentane wash to extract the wax from the fiber walls and porosify the walls;
2. A boiling methanol wash to extract most of the TEG from the core;
3. A Soxhlett extraction with pentane to remove the last traces of TEG from the core. Several more rapid pentane washes may suffice for this last step, instead of Soxhlett extraction, in which case the entire extraction procedure could be carried out continuously.

#### PROPERTIES

The yarns produced contain 10 fils with a total denier of

between 60 and 75, *i. e.*, an average denier of 6-7 denier/fil. The diameter of the individual filaments is  $\sim 0.002"$  (Figure 1), which, if they were ordinary solid and dense polypropylene filaments, would have deniers around 16. The low denier (a consequence of the low density of the filament) reflects the porous nature of the walls and the low



*Figure 1. Active Carbon-Filled Microporous Hollow Filament.*  
SEM Microphotograph. (X1500)

bulk density of the active carbon in the core. (The bulk density of the carbon as received is 0.25 gms/cc.) With respect to textile appli-

cations, the denier of the filaments appears satisfactory for fabric handle, but the yarn will probably have to be plied two or more times to make a strong fabric.

The tenacity values of different samples varied between 2.1 and 2.8 gms/denier with elongations to break between 20% and 30%. Samples which had undergone high shrinkage during extraction had lower tenacities, sometimes lower than 1.5 gms/den, with correspondingly high elongations, above 40%.

The porosity of the yarns is quite high. The permeability rate is about 3,000 gms/m<sup>2</sup> per day for water vapor and even much higher for organic substances, such as carbon tetrachloride and methanol. The higher permeability rate for organic liquids would be expected for a hydrophobic material such as polypropylene. It is highly probable that because of the fine pore structure and hydrophobic character of the polypropylene, although water vapor passes through the walls, liquid water will not. Thus body sweat, which attacks some active carbon fiber systems, will be prevented from reaching the active carbon components of these fibers by the polypropylene sheath.

The absorption capacity of the yarns for CCl<sub>4</sub> is generally about 40% and on some samples it has reached 48%. The best values apparently come from good control of extraction conditions and a high carbon loading in the filaments.

Sorption of a half-pound sample submitted to NARADCOM was about 40%, and this was made with a reduced carbon loading in the slurry to fore-stall any spinning problems. Therefore, 45% to 50% CCl<sub>4</sub> pick-up seems an attainable goal with relatively little further effort.

Dynamic absorption measurements (the report from Mine Safety Appliance Company is appended) also have shown high sorption characteristics sufficient for the goal of the project.

Thus, there has been attained a hydrophobic textile yarn of high absorptive capacity with excellent potential to make a rugged absorptive textile fabric.

#### YARN DEVELOPMENT

The preparation of the active carbon-filled microporous hollow multifil yarns required three areas of investigation. These were: the

core of active carbon, a suitably microporous and strong fiber wall, and the technology to combine these developments to produce fine yarns. In the following summary, the main developments in these three areas will be discussed.

#### Core Technology

Early in the program, high solids-loaded fluid slurries of active carbon were prepared and the absorptive activity regenerated. With these slurries, co-extrusion in the hollow fiber spinning system appeared to be the most promising method of obtaining a carbon-filled hollow fiber. Considerable effort had to be expended, though, to obtain an optimum slurry and also to develop the pumping and regeneration techniques required in its extrusion. The dispersions of highest loadings are made by passing the suspension of carbon in triethylene glycol through a colloid mill several times and adding additional carbon powder to the slurry as it recirculates in the mill. The flow characteristics of the slurries are complex. They will cease to flow because of too high or too low a shear rate. But within certain limits, pulverized samples (95% < 325 mesh) classified through a 200-mesh screen were pumped with a Zenith gear pump through our spinnerets for considerable times without noticeable interference with flow.

Maximizing carbon loadings of the slurry occupied intensive effort. The weight of carbon per volume of slurry is the property of concern from the extrusion standpoint, since the slurry is metered into the fiber by volume. The sorption capacity per volume of slurry is consequently the relevant test for regeneration of the activity and final efficacy of the slurry system.

Slurries of several different carbons in a variety of carrier fluids were investigated to obtain the highest absorption capacity, after regeneration, per volume of slurry. Slurries of Amoco PX21, a newly developed petroleum-based material, in triethylene glycol showed the highest

sorption capacity per cc of slurry by far, and especially so if the absorption measurements are carried out on carbons equilibrated with air of moderate humidity (Tables 1, 2, and 3).

Table 1. Carrier Fluid Testing of PX and XZ Carbons

A Carbon Type	B Carrier Fluid Type	C Carbon Weight (g)	D Carrier Fluid Wt. (g)	E Slurry Density (g/cc)	F Slurry Volume (cc)	G Pigment Density (g/cc)
PX21 <sup>a</sup>	TEG	2.7	10	1.27	10.0	0.27
PX21	TEG	2.8	10	1.20	10.7	0.26
PX21	Water	2.6	10	1.13	11.2	0.23
PX21	Freon E3	1.6	10	1.87	6.2	0.26
PX21	Xylene	3.2	10	1.04	12.7	0.25
PX21	LOPS*	2.9	10	0.99	13.0	0.22
PX24	TEG	6.5	10	1.30	12.7	0.51
PX24	Freon E3	3.9	10	1.67	8.3	0.43
PX24	LOPS*	7.0	10	1.09	15.6	0.45
PX24	Xylene	4.5	10	1.11	13.1	0.34
BC-XZ <sup>b</sup>	TEG	8.4	10	1.44	12.8	0.66
BC-XZ	Water	8.8	10	1.30	14.5	0.61

Columns C, D, and E, are measured:

$$F = \frac{C + D}{E};$$

$$G = C/F.$$

\*LOPS = Low Odor Paraffin Solvent, a refined kerosene from Ashland Chemical.

*a* = PX21, Amoco Corporation

*b* = BC-XZ, Barneby-Cheney Corporation

Table 2. Sorption Capacity of Activated Carbon Dispersions

Carbon	Dispersion Type	Sorption Medium	Sorption Capacity of Powder (wt Basis) (g CCl <sub>4</sub> /g)	Sorption Capacity of Dispersion, Vol. Basis (g CCl <sub>4</sub> /cc)
XZ	Bulk Powder	CCl <sub>4</sub>	0.51	0.23
		Air-CCl <sub>4</sub> *	0.4	0.2
	TEG†	CCl <sub>4</sub>	0.51	0.33
		Air-CCl <sub>4</sub> *	0.4	0.24
PX21	Bulk Powder	CCl <sub>4</sub>	2.10	0.63
		Air-CCl <sub>4</sub> *	2.09	0.63
	TEG†	CCl <sub>4</sub>	2.10	0.55
		Air-CCl <sub>4</sub> *	2.10	0.55
PX24F	Bulk Powder	CCl <sub>4</sub>		
		Air-CCl <sub>4</sub> *	0.69	0.39
	TEG†	CCl <sub>4</sub>		
		Air-CCl <sub>4</sub> *		

\*These experiments were carried out on samples dried under vacuum, then "equilibrated" with the atmosphere for several hours before testing. The sorption test was carried out in air saturated with CCl<sub>4</sub> vapor.

†After regeneration.

Table 3. Packing Factors of Activated Carbon Dispersions

Carbon	Dispersion Factor	Packing Factor
XZ	Air	0.35
	TEG	0.48
PX21	Air	0.52
	TEG	0.44
PX24	Air	0.61
	TEG	0.56

Qualification of the sorption efficacy of PX21 vis à vis carbon tetrachloride and dimethoxymethyl phosphonate (DMMP) was approved

by the Contracting Officer after submitting results of the investigation of its rate of sorption and sorption capacity (Figure 2.).

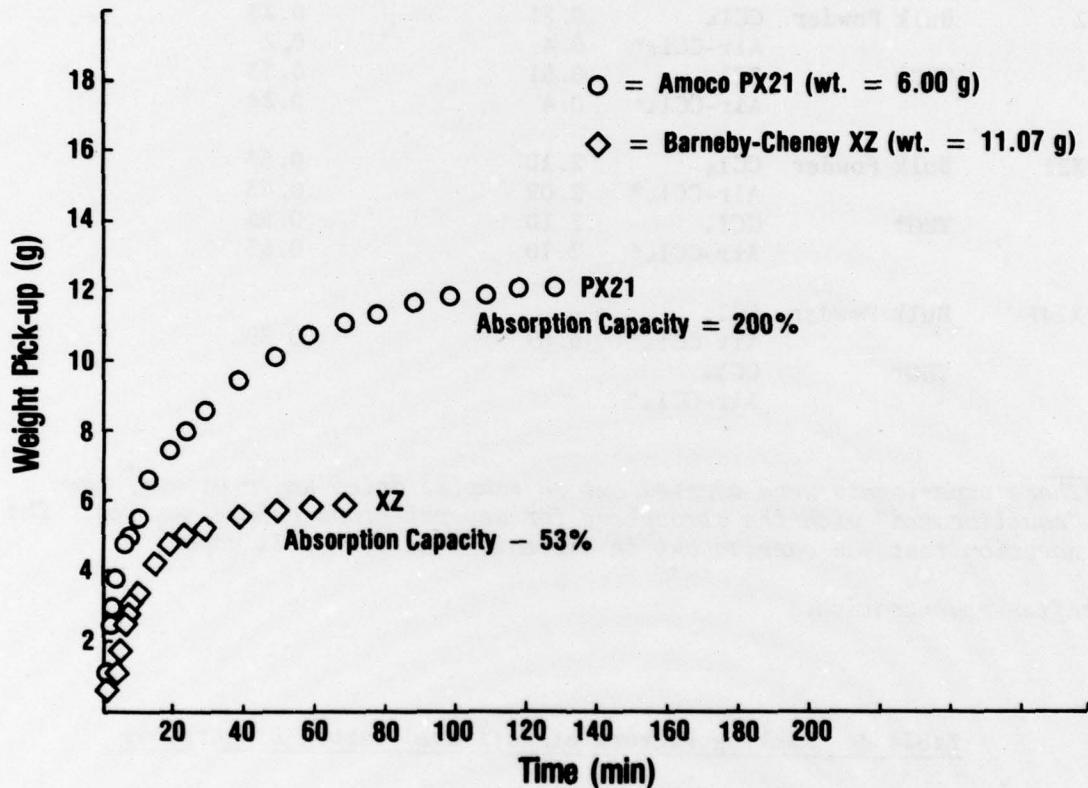


Figure 2. Sorption of Carbon Tetrachloride by Active Carbons

The measurements shown below (Table 4) for Amoco PX21 carbon show almost a 4:1 increase in  $\text{CCl}_4$  sorption capacity over Barneby-Cheney XZ carbon, and a similar increase for DMMP. Also, it is seen that the pore volumes, when calculated from the weights of the DMMP and  $\text{CCl}_4$  sorbed and the respective densities of the liquids, agree closely,

as seen in *Table 4*. Thus, the mechanism of the sorption appears similar for both carbons for the two sorbates, *i. e.*, both  $\text{CCl}_4$  and DMMP condense in the pores during sorption.

*Table 4. Sorption Capacities of Activated Carbons*

	CCl <sub>4</sub>		DMMP	
	Weight Pick-up (%)	Volume Pick-up (%)	Weight Pick-up (%)	Volume Pick-up (%)
Barneby-Cheney XZ	50.7	.33	40.9	.35
Amoco PX21	209	1.31	154	1.31

Considerations of maximum packing factors were included in our studies to help improve the solids loading of the slurries. The packing factor results were calculated from solids loadings, absorptive volumes of the carbons, and the densities of carbon and suspending fluids. The results give a good measure of the accessible void volume between the particles from which the potential for greater solids loadings was estimated. At 0.31 gms/cc solids loading (the maximum we achieved), PX21 is near its maximum solids loading and in air gives about 2.5 times the absorption capacity per cc of slurry of Barneby-Cheney XZ.

Much of the effort in developing a core material was spent on regenerating the carbon activity to its fullest extent. Complete regeneration of both Amoco PX21 and Barneby-Cheney XZ carbons was obtained from TEG slurries by several days' Soxhlett extraction of the TEG by methanol. More rapid regeneration of the activity was attained by Soxhlett extraction with pentane. However, to regenerate the carbon activity of large amounts of yarn wound on a spool, successive extractions were necessary because of the poor circulation within the yarn package. The yarn, wrapped over a layer of felt on a porous spool, is first extracted in a pentane bath, then in boiling methanol, again in pentane, and finally by a relatively short (overnight) Soxhlett extraction with pentane. The

order of extractions was chosen with the purpose of carrying out the following steps:

The fiber walls had been spun from a blend of polypropylene and wax, and the first pentane extraction porosifies fiber walls. On soaking in pentane, the wax is removed from the blend and the polypropylene wall becomes porous.

In the succeeding methanol bath, the methanol penetrates to the interior of the yarn and extracts most of the TEG from the core.

The remaining small amount of TEG is desorbed from the carbon by pentane, which is then readily removed under vacuum.

Some experiments to test the feasibility of extracting the drawn yarn in fabric form or as hanks showed that extraction of the fabric will also regenerate the carbon activity, although the fabric shrinks considerably. Nevertheless, this approach is probably the one to use for regeneration on a large scale. The fabric might be extracted at least partially on a continuous basis, or perhaps even completely, but further experiments on fabrics will have to be carried out to ascertain and develop the optimum conditions.

#### Microporous Hollow Fibers

The contract specifications for the hollow fiber were fine size, microporosity, and sufficient mechanical properties for textile processing and applications.

The approach chosen to spin fine denier filaments was to spin through relatively coarse spinneret holes and achieve the required fine deniers by high draw-down from the melt. The microporosity would be achieved by extraction of the hollow fiber prepared by phase separation spinning of a blend of polymer and an extractable component. Rheological and extraction studies showed that a blend of polypropylene with 30% wax was a satisfactory system. And there was a further benefit, in that the spinning temperature is much lower (170°C vs. 280°C for ordinary polypropylene spinning). From the blend, hollow fibers of fine denier and high porosity were readily obtained.

The porosity of the fiber walls was monitored by measuring the amount of fluid lost by evaporation from the fiber core with the fiber ends sealed. The fluid loss was determined by either weight loss of the filled fiber, in the case of slow diffusion, or by following the movement of the fluid meniscus in the core when the porosity was high. The rate of loss of fluid by permeation through the filaments was seen to be quite high. For example, the rate of water permeation is 3,000 g/m<sup>2</sup> per day, five times the rate called for in the contract. With carbon tetrachloride and methanol as the test fluids, the rate is more than ten times greater.

#### Filled Fiber Spinning

Co-extrusion of the polypropylene/wax together with the carbon slurry was carried out to spin both monofilament and multifilament hollow fiber yarns filled with the slurry. The extrusion conditions are much more critical than for extruding the polypropylene/wax blend as empty hollow fibers, although they are in a similar range. We found that at the exit of the spinneret, where polymer and slurry make contact, the slurry interacts with the polymer to change its rheological properties, and also affects the conditions in the spin line, *e. g.*, the cooling rates are much slower if the fiber is filled with the slurry.

Several spinnerets were used for the spinning. They included a specially-made monofil spinneret with straight-through flow for the slurry to augment its passage, and special pins for positioning the hollow needle. Also, a hollow filament multi-hole spinneret (12 holes, built earlier at FRL) was modified for co-extrusion of the slurry and fiber walls.

The yarns were extruded at 165° to 175°C down a 15-foot cooling stack at high draw-down ratios (>100:1) typical of usual spinning operations, to a take-up winder, and then drawn 5:1 in a separate step. The spinning conditions have still not been optimized sufficiently to give yarns of sufficient uniformity for high-speed fabric manufacturing processes, although staple yarn processes should offer little difficulty. Frequent thick sections of filament are encountered which give problems in

drawing. This unevenness was not encountered when the unfilled polypropylene/wax hollow filaments were spun, so that some deleterious interaction between the fiber and the slurry is still occurring. Nevertheless, multifilament yarn spin runs of up to two hours' duration were carried out, and about five pounds of as-spun fiber was wound up.

The as-spun fibers draw well, except for the thick sections, which introduce breaks, but again, the range of conditions is narrow. Too high a draw temperature interferes with the fiber absorptive properties, and too low a temperature results in fiber breaks. Drawing temperatures of 100°C appeared to be satisfactory for our yarns.

The yarns can be drawn either before or after extraction, but because the yarns, with their built-in lubricants, have much better handling characteristics before extraction, they are drawn before extraction.

#### Extraction and Regeneration

The techniques for extraction and regeneration of the yarns were described in an earlier section. Most of the effort was directed toward complete regeneration and only little work was done on finding the optimum extraction system. However, the results do show that most probably it will be practicable to carry out the extraction and regeneration on the fabric, *e. g.*, in baths, in continuous steps. It appears that with further investigation quite efficient and probably inexpensive extraction and regeneration systems can be developed.

The yarn sample after extraction showed  $CCl_4$  absorption values between 40% and 48%, based on the overall weight of the yarn, and the rates of absorption were quite high. In fact, they were higher than measurements with the active carbon bed. The higher rate for the yarns probably reflects a more accessible geometry of a fiber mat compared to the carbon bed and not any intrinsic absorption rate superiority of the yarn.

A report of a screening type dynamic absorption experiment by our subcontractor, Mine Safety Appliances, showed that the dynamic sorp-

tion characteristics of the yarn samples is also high and should be adequate for the goals of the project. The report is appended.

A microporous hollow multifilament was also produced as a control, and it showed surprisingly high absorption, about 9% pick-up of  $CCl_4$ , which should help the absorption capacity of the total yarn. A non-porous polypropylene hollow fiber showed negligible  $CCl_4$  pick-up.

The samples we extruded have about equal volumes of material in the core and in the walls. Thus, on a first approximation we lose only about half the strength of a solid fiber by replacing half the polymer volume in a fiber with carbon powder. Simple calculation will show that with a carbon bulk density of 0.25 gms/cc, about the density of the Amoco PX21 as received, and assuming the 200% absorption capacity the regenerated PX21 has shown, our fiber could be expected to absorb about 50% of its weight if completely filled with the active carbon powder. Thus, taking one cc of fiber, its 0.5 cc of carbon with a bulk density of 0.25 gms/cc will weigh 0.13 grams. Similarly, if we assume a density of about 0.8 gm/cc for the porous polypropylene, the cc of fiber will contain 0.40 gms of polypropylene, and the density of the fiber will be:

Carbon in 1 cc of fiber	=	0.13 gms
Polypropylene 1 cc	=	<u>0.40 gms</u>
Material in 1 cc	=	0.53 gms/cc of fiber.

The percentage of carbon in the fiber is then  $\frac{0.13}{0.53} = 25\%$  by weight, and the fiber will be expected to pick up 0.5 gms  $CCl_4$ /gm of fiber, or 50% absorption capacity (based on 200% absorption capacity of the regenerated carbon).

During the extraction, the yarn tends to shrink considerably, with a consequent loss in tenacity and increase in elongation. A comparison of the properties of the same drawn yarn extracted with free shrinkage as a loose hank and with shrinkage almost completely restricted (the sample was wound on a beaker) is shown in the following table:

Table 5. Effect of Restricting Shrinkage during Extraction\*

(Sample #2325-36)

	Denier	Tenacity (g/den)	Elongation (%)	Absorption (%)	CC14
Extracted with No Shrinkage:	68	2.4	22	39	
Extracted with Free Shrinkage:	103	1.0	43	43	

\*These data were obtained from a limited number of examples, but are believed to reflect the trend.

The shrinkage takes place primarily in the first pentane extraction and the fabric (or yarn) would have to be restricted from shrinking in that step to maintain tensile properties. Methods for mechanically stabilizing fabrics and yarns have long been in use in the textile industry, and these should be directly applicable to control the shrinkage of our fabrics or yarns.

Large samples were extracted as yarn while wound on soft spools. Because of the relatively large sample size, the local extraction conditions were under poor control, and in one case the spool completely collapsed during extraction. Thus, although the absorption capacity of 40% is substantial and surpasses the contract specifications, the mechanical properties are quite a bit lower than those of the yarn samples of smaller quantity which have been studied. We have routinely been obtaining yarns with between 2 and 2.5 g/den and 20% to 30% elongation to break. Nevertheless, even on these large samples, which are about 1.5 g/den, the mechanical properties are sufficient for textile processing, especially with the appreciable elongations of greater than 30%.

#### CONCLUSION AND RECOMMENDATIONS

The properties of the yarns, flexibility, moderate tenacity and elongation, and high sorption capacity for organic vapors, show excellent

promise that the yarns will fulfill the expectation that they are true textile yarns with high sorption capability. Small amounts of the yarns have already been knitted into swatches. However, it still remains to be demonstrated that satisfactory woven fabrics can be obtained using the yarns, which will require some further spinning of yarns and weaving into fabrics.

The technology of extraction with large amounts of yarn has to be developed and will probably be best carried out on the fabrics themselves.

Further along, optimization of the sorbency characteristics, mechanical properties, and fabric construction in the context of the desired CW protection requirements will have to be developed.

MEASUREMENT OF ADSORPTIVE CAPACITY OF  
CARBON-FILLED HOLLOW FILAMENT YARN

A. J. Juhola

Carbon Tetrachloride Test

The static test result for  $CCl_4$  was 39.3% by weight. The  $CCl_4$  reservoir was maintained at 0°C while the sample in the vacuum chamber was at 25°C. A correction was made for the weight of unadsorbed  $CCl_4$  in the weighing bottle. Without this correction the computed capacity would have been 41.6%. We are in essential agreement with your 40%.

DMMP Test

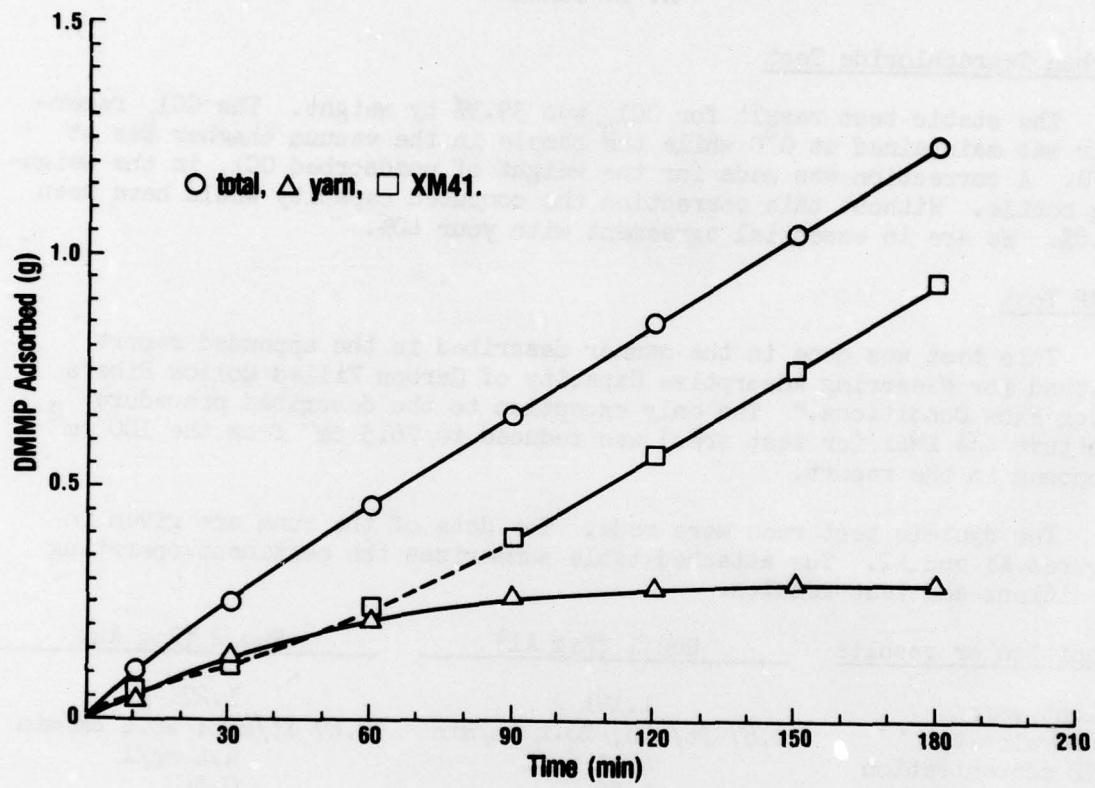
This test was done in the manner described in the appended report "Method for Measuring Adsorptive Capacity of Carbon Filled Hollow Fibers Under Flow Conditions." The only exception to the described procedure was that the XM41 (or test area) was reduced to 76.5  $cm^2$  from the 100  $cm^2$  proposed in the report.

Two dynamic test runs were made. The data of the runs are given in Figures A1 and A2. The attached table summarizes the pertinent operating conditions and test results.

Condition or results	Run 1 (Fig A1)	Run 2 (Fig A2)
Weight yarn	1.191 g	1.271 g
Face velocity	0.67 ft/min; 20.4 cm/min	0.67 ft/min; 20.4 cm/min
DMMP concentration	4.45 mg/l	4.4 mg/l
DMMP $P/P_0$	0.56	0.54
Time to equilibrate	150 min	150 min
DMMP capacity	0.253 g/g; 0.226 cc liq/g	0.228 g/g; 0.195 cc liq/g

On the liquid volume basis, the adsorptive capacity for  $CCl_4$  was 0.247 cc/g compared to the above 0.226 and 0.195 cc/g; i.e., more  $CCl_4$  is adsorbed than DMMP. This may be in part due to the smaller molar volume of  $CCl_4$  (97.5) compared to that of DMMP (106).

The yarn was retained between two stainless steel screens which were then secured by means of a staple at the screen center. It was impossible to distribute the yarn evenly because of its springiness. There were a considerable number of holes or open areas in the yarn layer through which the gas stream could then pass directly to the XM41 pad. Even then, 50% or more of the DMMP was adsorbed by the yarn over the first 60 to 70 minutes of exposure time. We cannot tell at this time whether the yarn could have adsorbed all the DMMP if it had been evenly distributed as it would be in a woven fabric.



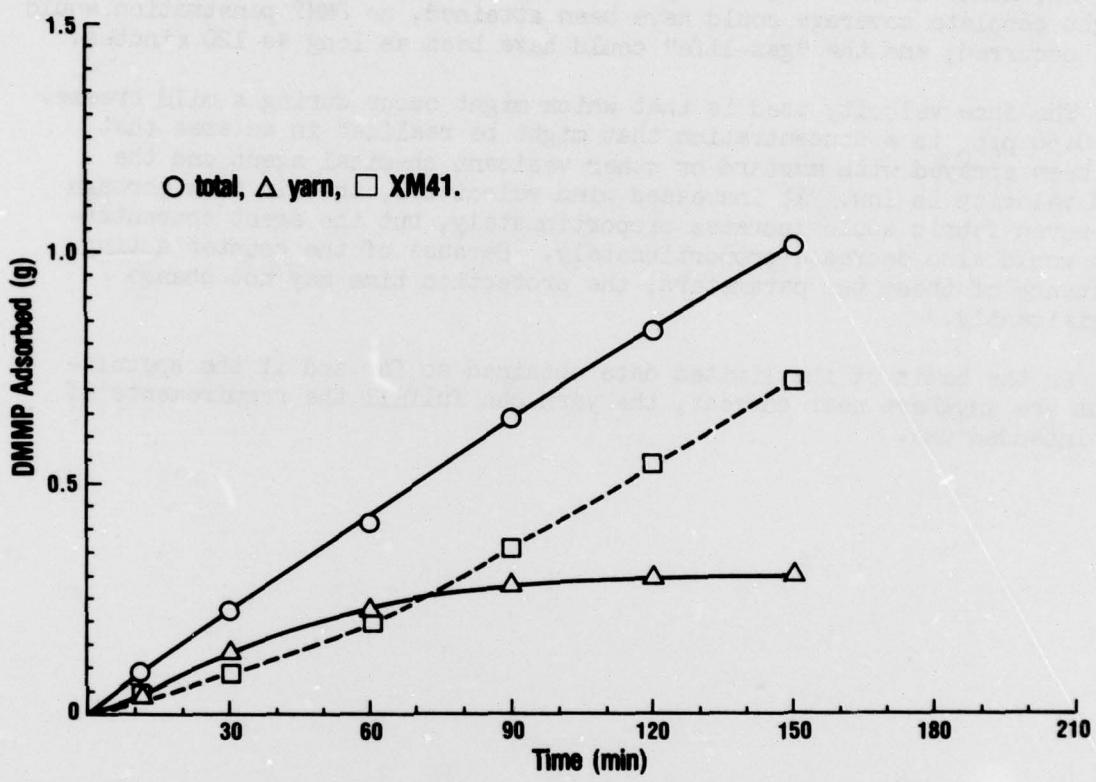


Figure A2 DMMMP Adsorption

The weight of the yarn was about that used in lightweight clothing, such as shirts. Military clothing, however, would be two to three times heavier, hence it is a distinct possibility that with three times the yarn weight complete coverage could have been attained, no DMMMP penetration would have occurred, and the "gas-life" could have been as long as 120 minutes.

The face velocity used is that which might occur during a mild breeze. The 0.56 p/p<sub>o</sub> is a concentration that might be realized in an area that had been sprayed with mustard or other vesicant chemical agent and the wind velocity is low. At increased wind velocities, the air flow through the woven fabric would increase proportionately, but the agent concentration would also decrease proportionately. Because of the counter acting influence of these two parameters, the protection time may not change significantly.

On the basis of the limited data obtained so far and if the speculations are anywhere near correct, the yarn can fulfill the requirements of the intended use.

METHOD FOR MEASURING ADSORPTIVE CAPACITY OF CARBON-FILLED  
HOLLOW FIBERS UNDER FLOW CONDITIONS

A. J. Juhola

Introduction

On an Edgewood Arsenal contract, No. DAAA15-70-C-0043 (1970), MSA Research Corporation conducted a "Study of Vapor Penetration Through Thin Carbon Layers." The objective of the study was to determine the change in effectiveness of carbon impregnated cloths against vesicant chemical agents when the carbon particle diameter and carbon loading were varied.

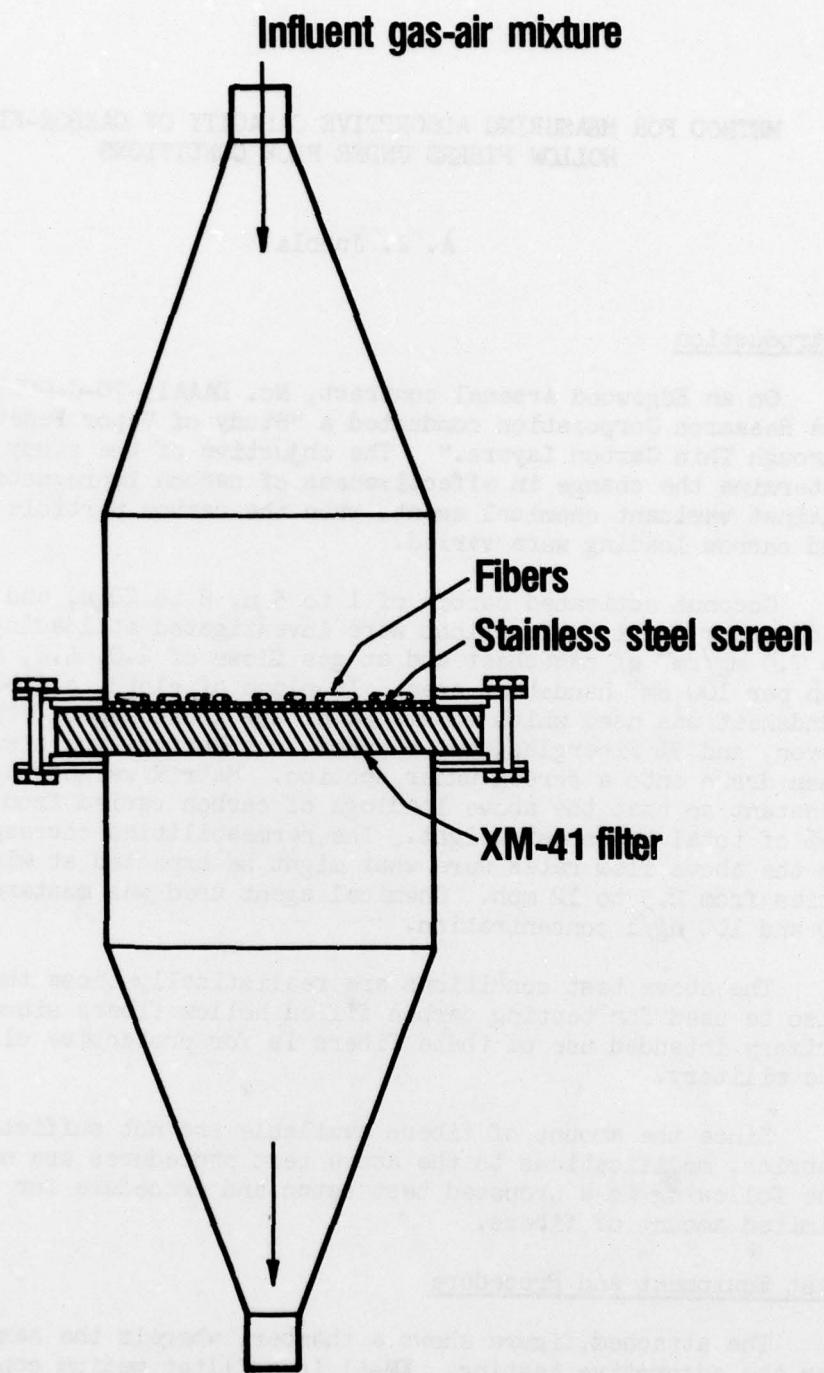
Coconut activated carbon of 1 to 5  $\mu$ , 8 to 20  $\mu$ , and 18 to 40  $\mu$  diameter particle fractions were investigated at loadings of 0.5 to 7.0 mg/cm<sup>2</sup> of handsheet and at gas flows of 2.0, 4.0, and 8.0 l/min per 100 cm<sup>2</sup> handsheet area. In place of cloth, a fiber matrix handsheet was used which consisted of 25% Kraft paper, 70% Viscose rayon, and 5% Fiberglas, wet-blended in a Waring-type blender, and then drawn onto a screen under suction. Matrix weight was held constant so that the above loadings of carbon varied from 4% to 35% of total handsheet weight. The permeabilities corresponding to the above flow rates were what might be expected at wind velocities from 2.5 to 12 mph. Chemical agent used was mustard gas at 50 and 100  $\mu$ g/l concentration.

The above test conditions are realistically those that should also be used for testing carbon filled hollow fibers since the primary intended use of these fibers is for protective clothing by the military.

Since the amount of fibers available are not sufficient to weave fabrics, modifications to the above test procedures are necessary. The following is a proposed test setup and procedure for testing a limited amount of fibers.

Test Equipment and Procedure

The attached figure shows a chamber, wherein the sample is placed for the adsorptive testing. XM-41 is a filter medium consisting of a fiber matrix and activated carbon. It has a long service time at the concentration level to be used for these tests. Placed above the XM-41



**Figure A3. Chamber for Dynamic Adsorption Testing of Carbon-Filled Hollow Fibers**

filter medium is a fine mesh stainless steel screen. The carbon filled hollow fibers are then laid on the screen. Area exposed to gas flow is 100 cm<sup>2</sup>.

Prior to the gas test, pure dry air is passed through the test chamber until the fibers and filter media come to constant weight. For the test, an appropriate organic vapor is metered into the air stream to give a low vapor concentration. After a predetermined time, the fibers and media are weighed separately. The total weight gain divided by the total flow gives the vapor concentration. The fibers cover a certain area as calculated from fiber diameter and length, and associated with this fiber coverage is a certain amount of vapor adsorption. One can now estimate the amount of adsorption for different fractional coverages of the chamber area. If the calculated amount adsorbed for the area, estimated for a woven fabric, is equal to the total amount experimentally measured, then there would have been no penetration through the fabric. The experiment can then be continued until a penetration is indicated by the calculations. The exposure time would then be the gas life at the initially chosen flow rate and concentration. If a penetration is calculated on the first weighing, then a new set of test conditions would have to be chosen.

#### Selection of Test Agent and Test Conditions

The test conditions used in the mustard tests can be used as guide for selecting the test agent and initial test conditions. A layer of 25  $\mu$  I.D. filaments, six filaments deep, and covering 80% or 80 cm<sup>2</sup> of the test chamber area would have about 0.3 g of carbon. On the hand-sheet test, with a carbon loading of 0.29 g of carbon, the mustard gas life was 115 minutes at a flow rate of 4 l/min and mustard concentration of 100  $\mu$ g/l. The adsorptive capacity of the carbon was 0.44 g/g for a coconut carbon. A nontoxic chemical that comes closest to mustard in its properties, which then could safely be used for these tests, is dimethoxymethylphosphonate (DMMP). Their pertinent properties are given below for comparison.

<u>Compound</u>	<u>Formula</u>	<u>Molecular weight</u>	<u>Den., g/cc</u>	<u>Molar Volume</u>	<u>Vapor Press @ 25°C mm Hg</u>
Mustard	$(ClCH_2CH_2)_2S$	125	1.07	117	1.4
DMMP	$CH_3O - P = O - CH_3$	124	1.17	106	1.2

DMMP is also a simulant for nerve agents; hence, the test results will be meaningful in regard to the expected application.